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Oxygen Isotopes in Atmospheric Sulfates, Sulfur Dioxide, and Water Vapors Field Measurements, July 1975

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Ecological Research Series

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Concerted variations in isotopic and concentration results were found for the three sites, demonstrating an apparent regional impact on the quality and quantity of particulate sulfate in the atmosphere. At all three sites, the oxygen-18 enrichments in suspended sulfates clearly varied inversely with sulfate concentration. This variation suggests that sulfates in cleaner air may have a different origin than sulfates in more polluted air masses. Samples collected during a period of local thunderstorm activity showed an abrupt increase in the oxygen-18 composition of particulate sulfate, but little effect on the isotopic composition of ambient water vapor.

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by

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SECTION 1

INTRODUCTION

The workability of various strategies for the control of sulfur dioxide and sulfate levels in the environment depends to a large degree on the transport and transformation of these materials in the atmosphere. Experimental results obtained in the Chemical Engineering Division (CEN) at Argonne National Laboratory (ANL) strongly suggest that measured oxygen isotope ratios for sulfate oxygen can be used to help distinguish between the two most likely mechanisms of sulfate formation in the atmosphere (1,2). Oxygen isotope ratios are customarily reported in del units (‰) which are a measure of deviation in parts per thousand from Standard Mean Ocean Water (SMOW). The concept of determining sulfate formation mechanisms from oxygen isotope ratios is based on the following experimental observations:

1) The oxygen isotope ratios for atmospheric water (-15 to -25‰) and air oxygen (+23‰) are significantly different.

2) The rate of oxygen exchange between sulfates and water is extremely low.

3) Sulfates formed in the laboratory by dissolution of SO_2 in water and subsequent oxidation by air to sulfate appear to consistently yield sulfate comprising three oxygens resulting from isotopic equilibration between SO_2 and water before oxidation and one oxygen originally associated with the oxygen in air (3).

4) Sulfate formed in the laboratory by oxidation of SO_2 to SO_3 and subsequent dissolution in water to form sulfate yields a sulfate enriched in ^{18}O compared with that produced as described in item 3 above.

Thus, sulfates formed by different mechanisms from the same SO_2, water, and air apparently can differ significantly in oxygen isotope ratio. As noted, the ^{18}O enrichment of atmospheric water and oxygen are significantly

different so that they can be easily distinguished; moreover, once formed, sulfate does not undergo oxygen exchange so that the formation mechanism is permanently reflected in the sulfate oxygen isotope ratio. To examine the formation mechanism of sulfate, it is, in principle, only necessary to sample simultaneously the sulfate, sulfur dioxide, and water vapor present in a given air mass and to measure the oxygen isotope ratios for each substance. Because of natural fractionation processes, the ^{18}O enrichment of atmospheric water is seasonally variable. As determined by analytical results on 24-hour samples that were collected on 3 consecutive days each month for 16 months at Argonne, the variations in the ^{18}O enrichment of particulate sulfate did not follow the observed seasonal variations in the ^{18}O of ambient water vapor (3). It might be assumed, however, that if atmospheric sulfate aerosols are secondary particles formed by hydrolysis of SO_2, either before or after oxidation, the ^{18}O enrichment of the sulfate should have a seasonal quality that is proportional to the number of water oxygen atoms incorporated into the sulfate molecule.

This report gives the oxygen isotope results obtained on 12-hour diurnal samples of aerosol sulfate, sulfur dioxide, and water vapor which were collected simultaneously at Auburn and Glasgow, IL, and on 24-hour samples collected simultaneously at St. Louis, MO, July 21-28, 1975. The purpose of the experiment was to test for correlation of the isotopic quality of aerosol sulfate with that of water vapor in sequential samples collected over a period of 6 days, and to see whether changes in isotopic quality were related to local or regional effects. The three sampling stations, Fig. 1, were located about 100 km apart. The St. Louis station was on the campus of Washington University; the Auburn and Glasgow stations were in rural areas.

Figure 1. Location of sampling sites: St. Louis, MO; Auburn, IL; and Glasgow, IL

SECTION 2

CONCLUSIONS

Some of the more significant conclusions from the experimental results described in this report are presented below.

1) The concerted variations in concentrations and in isotopic qualities of atmospheric sulfate and sulfur dioxide at the three sampling sites indicate that sulfur pollution was distinctly regional in nature.

2) Meteorological conditions had a marked effect on the isotopic quality and concentration of atmospheric sulfates.

3) The variations in oxygen isotope ratio of aerosol sulfate did not correlate well with that of ambient water vapor, indicating that, within the air masses under observation, the aerosol sulfate had an insignificant contribution of oxygen from the ambient atmospheric water.

SECTION 3

RECOMMENDATIONS

The results and observations of this report suggest that the following projects need to be carried out:

1) Repeat the reported experiment on atmospheric sulfates and water vapor by sampling simultaneously at three sites, over a period of two weeks or more, preferably under a set of weather conditions different from that of the reported experiment. The results would be valuable for confirming or modifying the conclusions drawn from the reported experiment.

2) Repeat the experiment, sampling upwind and downwind of a well-defined, substantial source of SO_2, such as an isolated industrial emitter. The results would be expected to reflect the influence of the localized strong source of SO_2.

3) Perform oxygen isotope analyses on samples of sulfur oxides taken directly from the emission stacks of typical power plants and refineries. Compare the isotopic results on such primary (freshly emitted) oxides of sulfur to those of ambient oxides simultaneously sampled in a region several kilometers downwind. If the isotopic quality of the ambient sulfates in the selected region are found to differ isotopically from that of the primary sulfates of the strong emitter, it might be concluded that ambient sulfates are made up predominantly of secondary particles.

SECTION 4

EXPERIMENTAL PROCEDURES

SAMPLE COLLECTION

Particulate sulfate samples and ambient sulfur dioxide samples were collected simultaneously in a filter pack, mounted in a hi-vol air sampler [sulfates on a top, 20 x 25 cm (8 x 10 in.), glass-fiber filter and the SO_2 on a bottom, K_2CO_3-glycerol-treated, cellulose fiber filter]. Ambient water vapor was concurrently sampled by drawing a stream of air through a cold trap (-80°C) located near the hi-vol air sampler. Consecutive sets of samples of sulfates, SO_2, and water vapor were collected each day at about 2 meters (6 feet) or more above ground level.

SAMPLE ANALYSIS

Sulfur dioxide samples collected on K_2CO_3-glycerol filters were air-oxidized to sulfate. These and the particulate sulfate samples were converted quantitatively to $BaSO_4$ by conventional methods. Each $BaSO_4$ sample was filtered into a porous graphite cup in which the oxygen was converted to CO_2 by high-temperature, high-voltage techniques (4). The ^{18}O analysis of the CO_2 was made on a high-precision isotope-ratio mass spectrometer (Model NAA-RM57 of Nuclide Corporation, State College, PA, with modified electronic circuits and gas-inlet system (5).

Water samples were converted quantitatively to H_2 and CO by reaction with hot graphite. The hydrogen was discarded through a palladium membrane and the CO was disproportionated to carbon and CO_2 by high-voltage discharge for subsequent mass spectrometric analysis of the CO_2 (4).

SECTION 5

RESULTS

Measurements of oxygen isotope ratios are reported for aerosol sulfates, the sulfates resulting from collection and air oxidation of atmospheric SO_2 on K_2CO_3-glycerol-treated paper filters, and water-vapor samples. Concentration data, presented in the form of collection rates (μmole/hr, assuming that the three hi-vol air samplers were each operated at a constant air flow rate throughout the sampling period), are reported for aerosol sulfates and sulfates resulting from SO_2 collection.

Isotopic and concentration data are given in Table 1 and in Figs. 2 through 12. Figures 2-4 show intersite comparisons of the isotopic results for particulate sulfate, sulfate formed by SO_2 collected on the alkaline filters, and ambient water vapor. Figures 5 and 6 show intersite comparisons of concentration results (expressed in terms of collection rate) for particulate sulfate and sulfate formed by SO_2 collection. Figures 7-9 give all the sulfur results obtained at each of the three sites, and Figs. 10-12 show the variations in isotopic results with concentration (collection rate) of aerosol sulfate at each site. (In the figures showing sampling dates, each numbered tick represents the beginning of the indicated day, *i.e.*, midnight.)

TABLE I. ISOTOPIC AND CONCENTRATION (COLLECTION RATE) DATA

Location	Sampling Date July 1975		Sulfate Aerosol		Sulfate from SO_2 on K_2CO_3 Filter		Water Vapor
	Start (hr/day)	Stop (hr/day)	Collection Rate (μmol/hr)	^{18}O (‰)	Collection Rates (μmol/hr)	^{18}O (‰)	^{18}O (‰)
St. Louis	19:30/21	10:10/23	4.3	7.3	19.7	10.2	-7.5
	10:15/23	11:35/24	1.7	14.2	15.0	11.6	-6.0
	11:40/24	7:35/25	2.2	7.9	1.4	5.2	-10.1
	7:45/25	15:00/26	8.6	5.3	37.7	13.1	(a)
	15:00/26	13:15/27	10.4	3.4	33.8	10.5	(a)
	13:20/27	15:30/28	8.7	7.6	39.1	13.8	(a)
	15:45/28	8:00/29	9.0	7.5	23.5	12.1	(a)
Auburn	7:00/22	16:30/22	6.4	9.2	72.2	10.3	-2.8(b)
	16:45/22	5:15/23	8.9	2.6	5.5	12.1	-5.0
	5:25/23	16:40/23	9.5	7.1	17.7	12.4	-7.2
	16:45/23	5:45/24	2.1	15.0	7.5	13.7	-8.4
	6:00/24	17:10/24	3.7	10.5	2.2	15.1	-9.1
	17:15/24	5:10/25	3.2	7.8	1.8	12.8	-7.5
	5:25/25	16:25/25	7.4	3.8	9.0	10.5	-10.1
	16:30/25	5:00/26	6.0	6.1	7.7	11.4	(c)
	5:00/26	16:30/26	5.8	2.9	9.2	11.1	-10.1
	16:30/26	5:10/27	6.7	3.5	4.7	8.4	4.6(b)
	5:10/27	16:30/27	8.5	7.4	8.5	8.8	-9.9
	16:30/27	5:00/28	6.1	8.5	3.1	11.9	-9.4
Glasgow	10:00/22	18:30/22	8.1	1.6	15.0	8.8	-0.4(b)
	18:45/22	7:40/23	7.8	7.1	2.5	9.9	-6.6
	8:00/23	18:40/23	5.3	11.8	12.4	12.5	-8.0
	18:40/23	8:00/24	2.7	19.8	1.3	16.7	-7.6
	8:00/24	19:10/24	3.7	12.6	3.0	6.1	-10.9
	19:15/24	7:15/25	2.5	15.1	0.7	42(d)	-8.3
	7:25/25	18:30/25	4.4	8.5	3.2	6.7	-11.2
	18:55/25	6:55/26	3.7	14.1	0.6	32.4(d)	-10.9
	7:10/26	18:30/26	7.7	5.7	18.5	13.4	-13.0
	18:30/26	7:00/27	8.8	6.9	14.0	13.5	-6.5
	7:00/27	18:30/27	6.1	12.9	3.1	3.5	12.0(b)
	18:30/27	6:30/28	4.8	15.3	1.6	17.9	-8.6

(a) Sample was not collected.

(b) Sample was damaged by partial evaporation during storage.

(c) Sample was lost.

(d) Sample was too small to obtain a reliable mass spectrometric analysis.

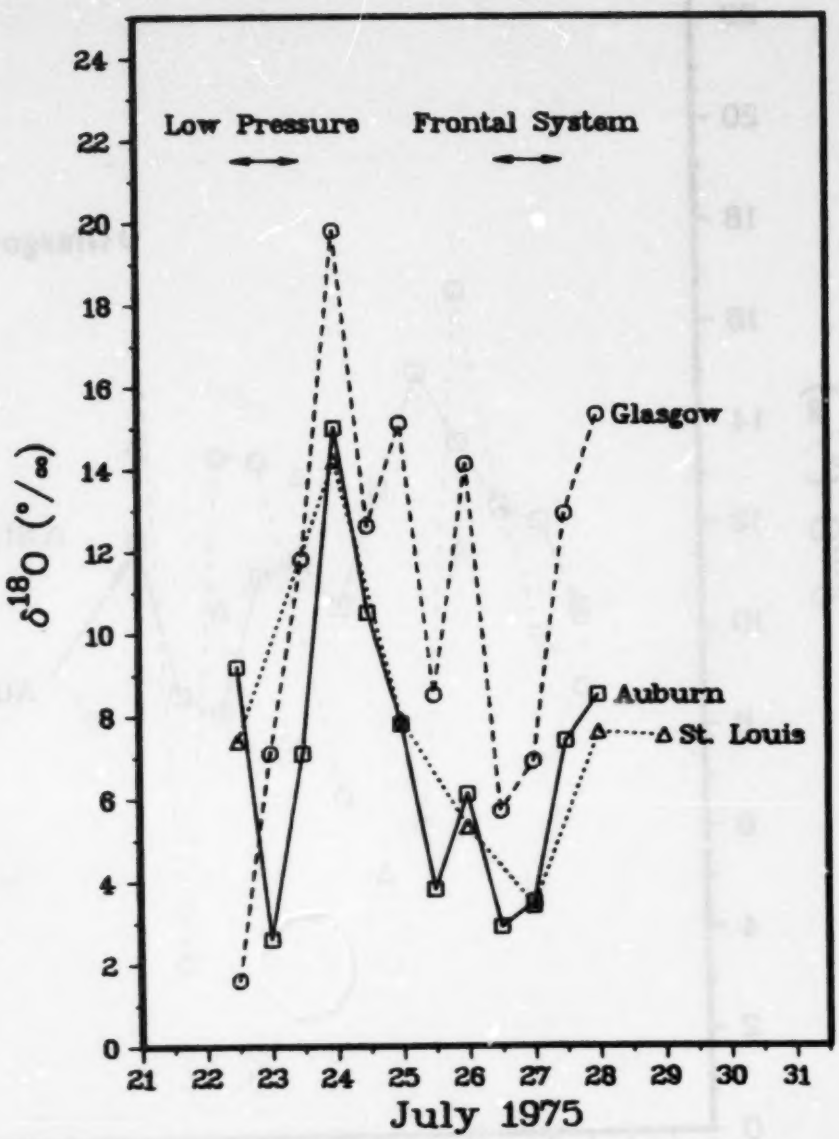

Figure 2. ^{18}O enrichment in aerosol sulfate vs. sampling dates at the three sites near St. Louis

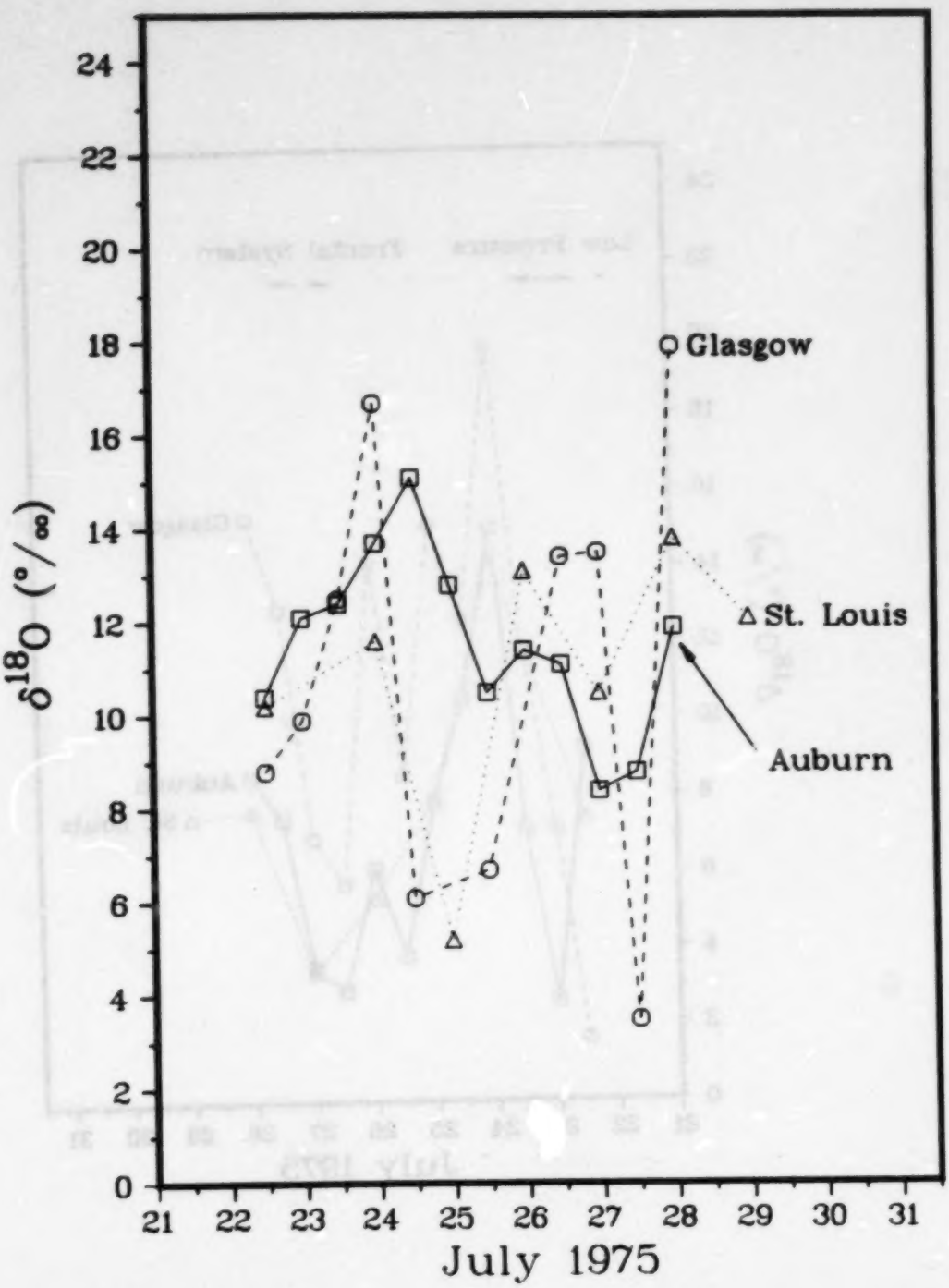

Figure 3. ^{18}O enrichment in sulfate formed from SO_2 gas at the three sites

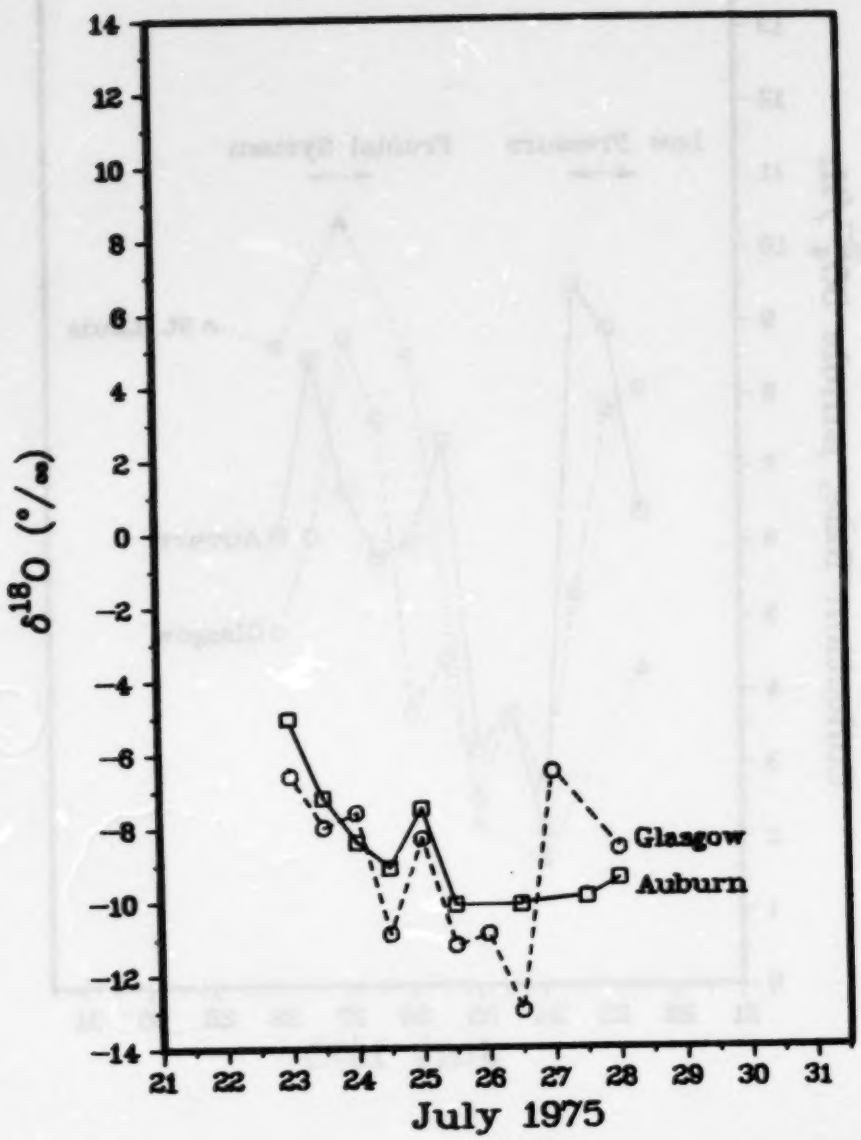

Figure 4. ^{18}O enrichment in water vapor vs. sampling dates at the three sites

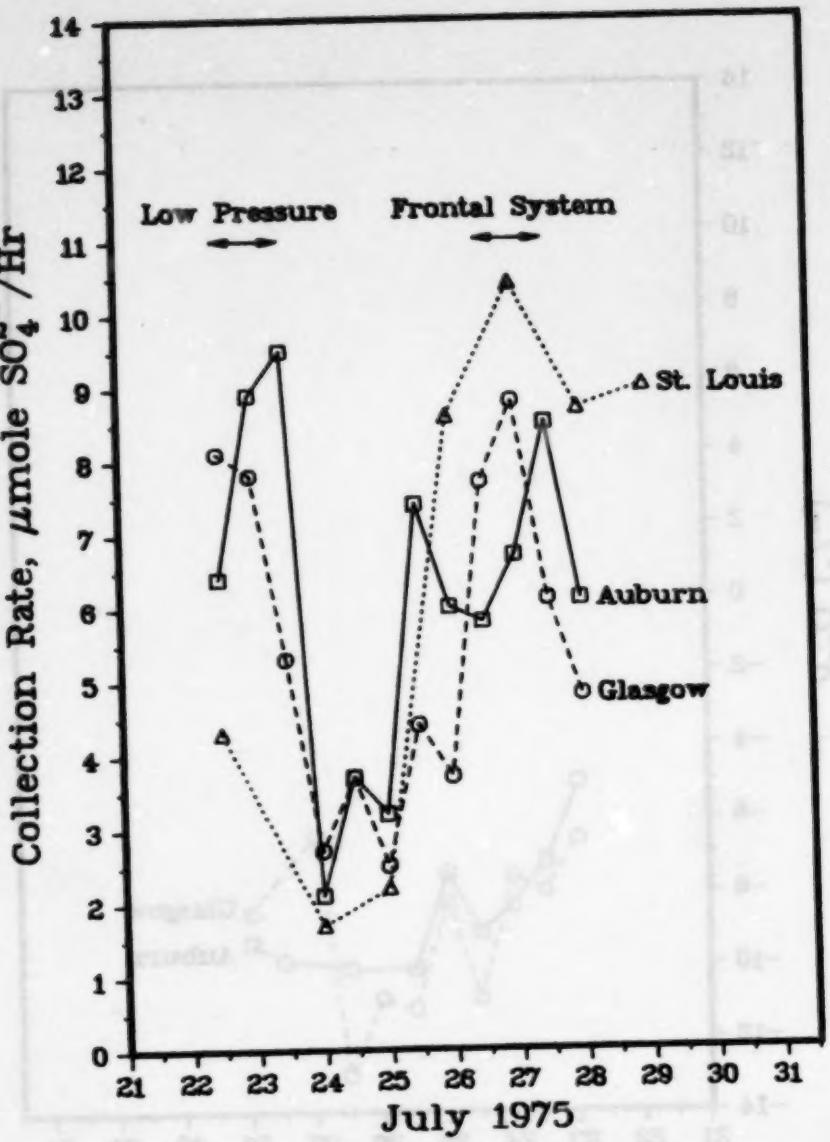

Figure 5. Aerosol sulfate collection rate at the three sites vs. sampling dates

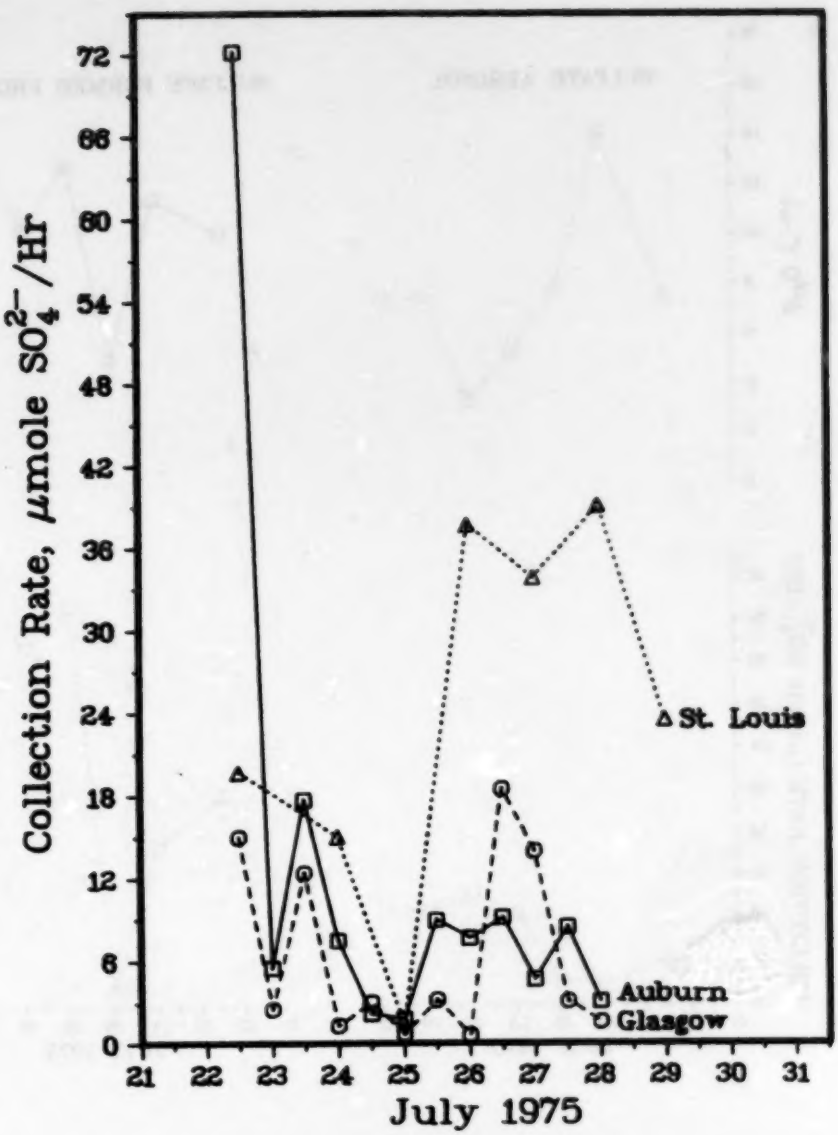

Figure 6. Collection rate of SO_2 (expressed as $SO_4^{=}$) at the three sites vs. sampling dates

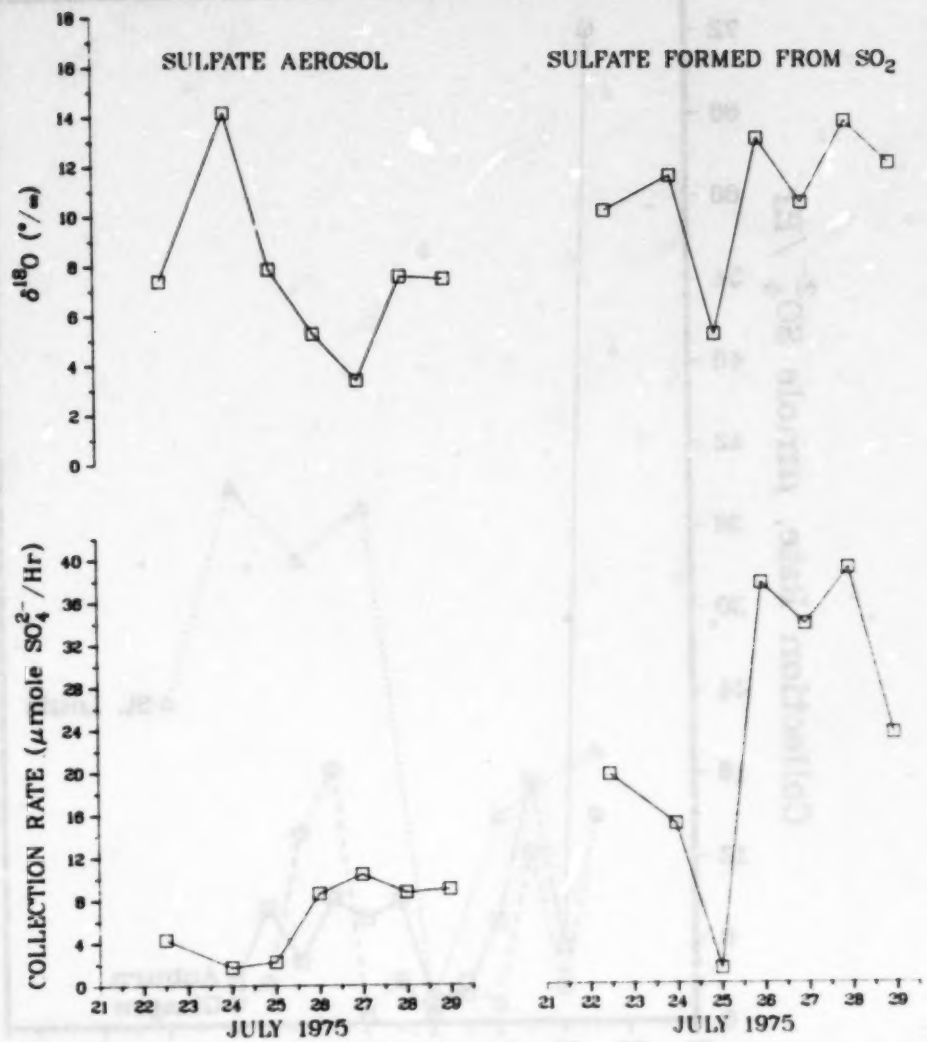

Figure 7. Collection rate and ^{18}O enrichment of aerosol sulfate and SO_2^- derived sulfate at St. Louis, MO

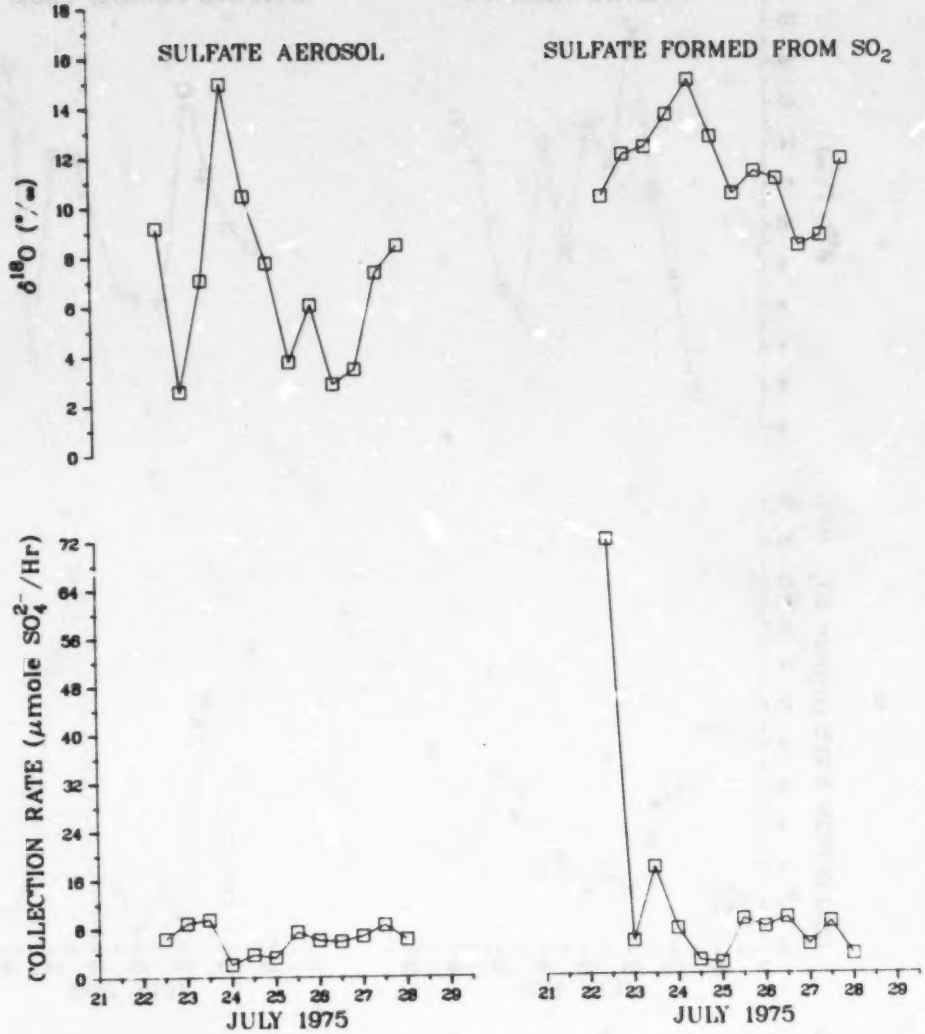

Figure 8. Collection rate and ^{18}O enrichment of aerosol sulfate and SO_2^- derived sulfate at Auburn, IL

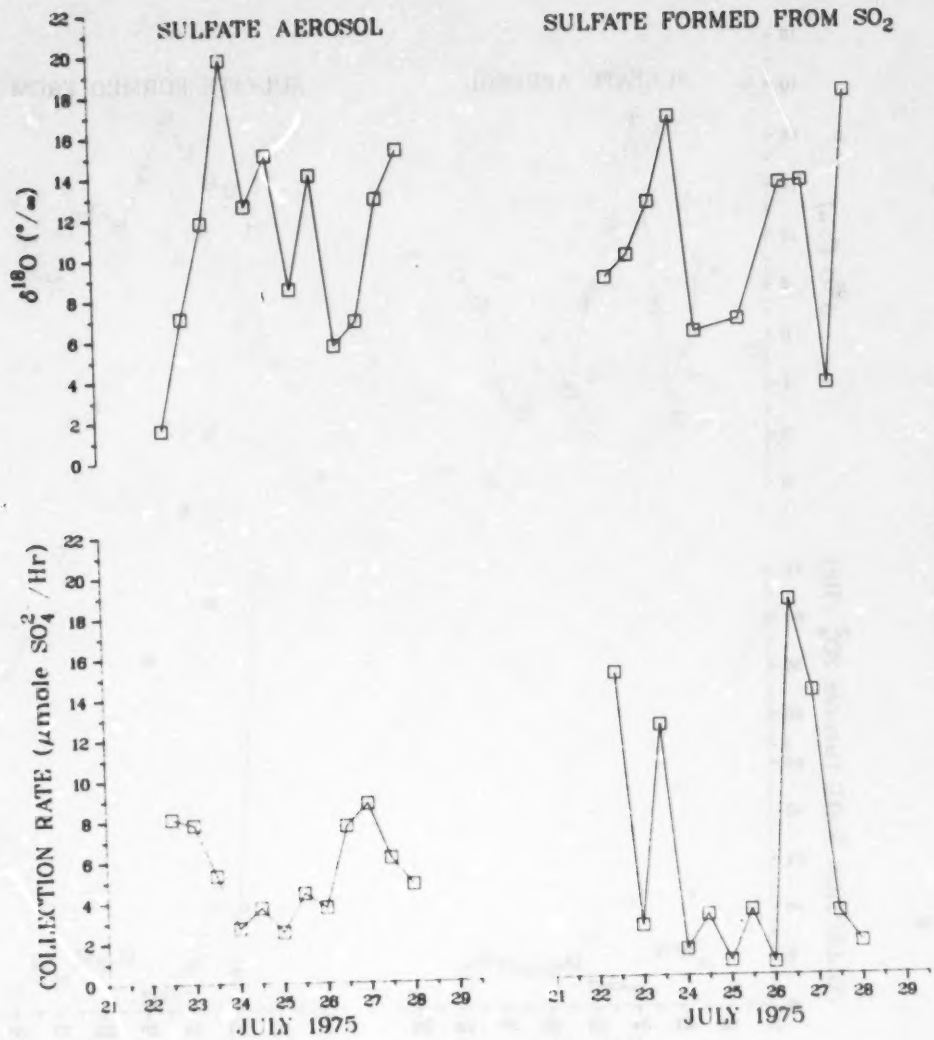

Figure 9. Collection rate and ^{18}O enrichment of aerosol sulfate and SO_2^- derived sulfate at Glasgow, IL

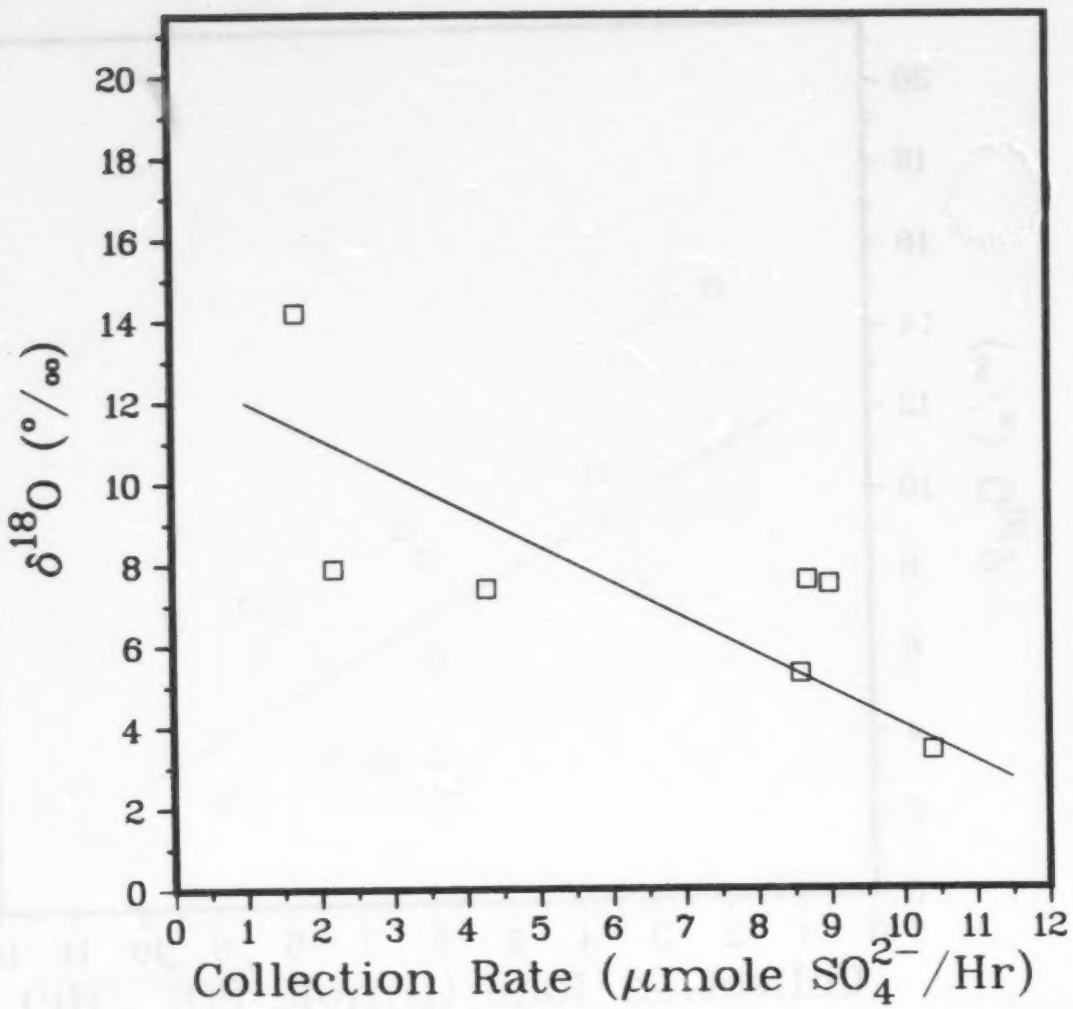

Figure 10. ^{18}O enrichment vs. collection rate of aerosol sulfate collected at St. Louis, MO

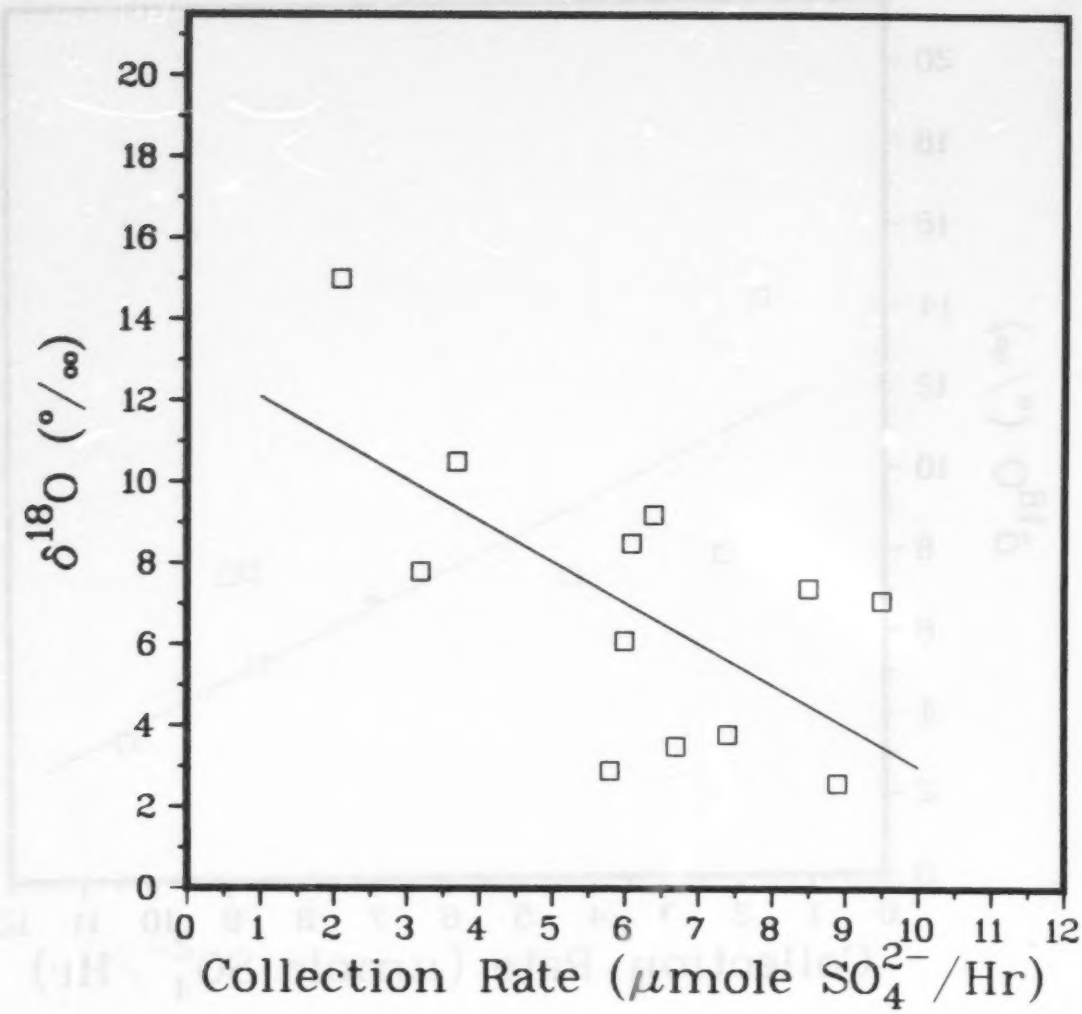

Figure 11. ^{18}O enrichment vs. collection rate of aerosol sulfate collected at Auburn, IL

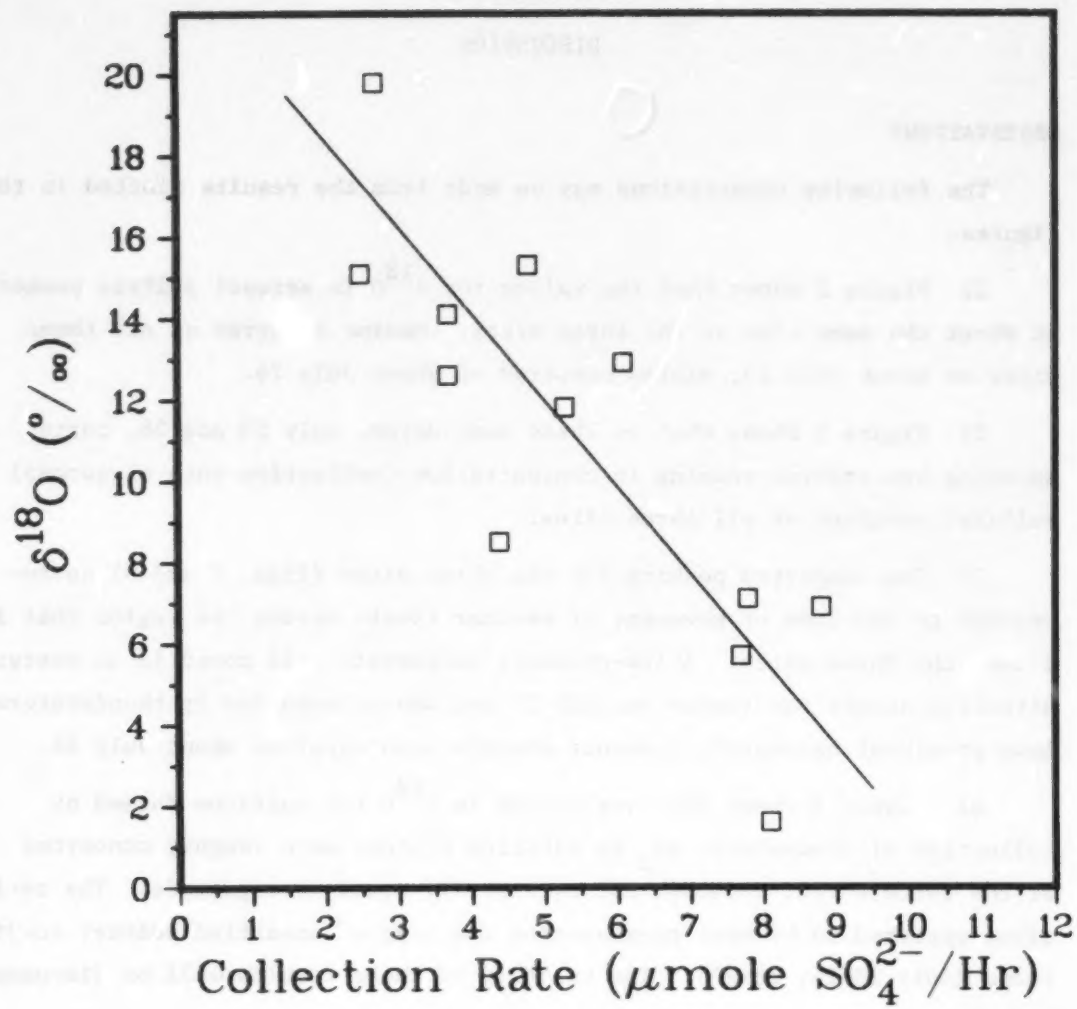

Figure 12. ^{18}O enrichment vs. collection rate of aerosol sulfate collected at Glasgow, IL

SECTION 6

DISCUSSION

OBSERVATIONS

The following observations may be made from the results plotted in the figures.

1) Figure 2 shows that the values for $\delta^{18}O$ in aerosol sulfate peaked at about the same time at the three sites. Maxima occurred at all three sites on about July 23; minima occurred on about July 26.

2) Figure 5 shows that on these same dates, July 23 and 26, corresponding but inverse peaking in concentration (collection rate of aerosol sulfate) occurred at all three sites.

3) The concerted peaking for the three sites (Figs. 2 and 5) corresponded to the time of movement of weather fronts across the region that includes the three sites. A low-pressure barometric cell moved in an easterly direction across the region on July 23 and was accompanied by thunderstorms. Less prominent barometric pressure changes also occurred about July 26.

4) Figure 3 shows that variations in $\delta^{18}O$ for sulfates formed by collection of atmospheric SO_2 on alkaline filters were roughly concerted at the three sites, although not necessarily equal in magnitude. The variations appeared to be most prominent on the days of unsettled weather conditions (July 23-24, 26-27). The validity of these results will be discussed later.

5) Figure 6 shows that the concentrations of SO_2 (expressed as collection rate) apparently dropped to near zero at all three sites immediately after the low pressure cell, accompanied by thunderstorms, passed over the region on July 23-24. (The unusually high value for the Auburn sample on

July 22 coincided with a northeast wind, blowing from the direction of a large power plant in Springfield, IL.)

6) In Fig. 4, a general downward trend in the ^{18}O content of water vapor is evident for the three sites during the first 3 to 4 days of sampling. The local thunderstorm that occurred on about July 23-24, accompanied by abrupt reductions in concentrations of sulfates and SO_2 and corresponding increases in the ^{18}O del values of sulfates, apparently had very little effect on the isotopic content of the atmospheric water vapor.

The 12-hour overnight samples of water vapor were often higher in $\delta^{18}O$ than the associated 12-hour day samples. This may have been caused by a higher contribution of ground water to ambient water vapor, through evaporation from soil and evapotranspiration from plants, at night when air movement was generally at a minimum. This was a ground-level sampling problem, its effects probably being most prominent in the overnight sample at Glasgow on July 26-27.

7) Figure 7 indicates that while the oxygen del values for aerosol sulfate in St. Louis varied inversely with the concentration parameter (correlation coefficient = -0.750, Fig. 10), the del values for the sulfates formed from collected SO_2 apparently varied directly with the SO_2-concentration parameter (correlation coefficient = 0.837). (Note the relative magnitudes of the collection rates of particulate sulfate and SO_2.)

8) Figure 8 shows an inverse $\delta^{18}O$-concentration relationship for sulfate aerosol in Auburn (correlation coefficient = -0.639, Fig. 11), but no significant correlation (correlation coefficient = -0.248) in the $\delta^{18}O$-concentration relationship for SO_2.

9) Figure 9 indicates that for Glasgow the $\delta^{18}O$-concentration relationships are inverse for sulfate aerosol (correlation coefficient = -0.841, Fig. 12) and only very weakly so for SO_2 (correlation coefficient = -0.320).

These observations give substantial support to postulates that (1) the fluctuations in concentration and isotopic quality of aerosol sulfate were regional phenomena; (2) both local and continental meteorological changes had important effects on the quality and concentration of atmospheric sulfate

within the region; and (3) the aerosol sulfate was not necessarily formed from the water that was carried by the air masses from which it was collected.

REGIONALITY

The regional character of the variations of both the isotopic quality and the concentrations of atmospheric sulfates and SO_2 is shown by the concerted peaking of these parameters at St. Louis, Auburn, and Glasgow (Figs. 2-6). If the origin of the pollutants at Auburn and Glasgow had been primarily the urban plume of St. Louis, the effect of a time lag should have been evident in the results. Likewise, local sources of sulfur pollution near either Auburn or Glasgow would not have produced the observed concerted pattern for all three sites.

METEOROLOGICAL EFFECTS

The apparent marked effects of local weather, on July 23 and 24, and of continental air movements, on July 26 and 27, demonstrate the impact that meteorological changes can have on atmospheric sulfur, apart from possible coincidental variations in emissions and/or transformations.

DISTINGUISHABLE SULFATES

The pronounced negative correlation between $\delta^{18}O$ and concentration of sulfate aerosols at all three sites, in connection with local weather disturbances (Figs. 2, 5, 7-12), suggests that as sulfate was removed from the atmosphere, the residual sulfate had a different isotopic character. Isotopic fractionation of oxygen in sulfates caused by partial removal is unlikely, however, because sulfate is relatively inert to isotopic exchange with water in which it is dissolved. A possible explanation for the negative correlation is that the sulfate contained in the air, after the thunderstorm disturbance, was transported trom higher altitudes by turbulent mixing. The high-altitude sulfate may have had a different origin (possibly a different mechanism of formation) from that of the low-altitude sulfate.

EQUILIBRATION OF SO_2 WITH WATER VAPOR

On comparison of the data in Figs. 3 and 4, it might appear that the lack of positive changes in SO_2 (monitored as sulfate on the alkaline filters) and water vapor at Auburn and Glasgow suggests a lack of perceptible

equilibration of oxygen isotopes between the SO_2 and atmospheric water in the air masses from which they were collected, although SO_2 might be expected to approach isotopic equilibrium with water in the atmosphere in a manner similar to the CO_2-H_2O system (6).

The validity of the herein reported isotopic data for SO_2 has been placed in considerable doubt, however, by subsequently performed, but yet unreported, experimental results obtained on blends of SO_2 of various ^{18}O enrichments. The results of these later experiments indicate that isotopic exchange between the moist reagents on the K_2CO_3-glycerol-treated filters and the collected SO_2, prior to oxidation to sulfate, can seriously impair the isotopic fingerprint of the SO_2. For this reason, the reported SO_2 results are probably not applicable to the determination of equilibration between SO_2 and water in the atmosphere.

ORIGIN OF AEROSOL SULFATE

If significant portions of the aerosol sulfate collected and analyzed in this experiment had been formed by SO_2-water reactions (either before or after oxidation of the sulfur) in the air masses from which they were collected, a component of the isotope variations in the aerosol sulfate might be expected to track that of the water vapor with an amplitude of at least one-fourth that of the water vapor. The apparent lack of positive correlation between the isotope variations in aerosol sulfate and water vapor at both Auburn and Glasgow suggests that the aerosol sulfate was not formed predominantly from the water in the air masses from which it was sampled.

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